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Toxicity and Bioavailability of Metals in the Missouri River Adjacent to a Lead Refinery

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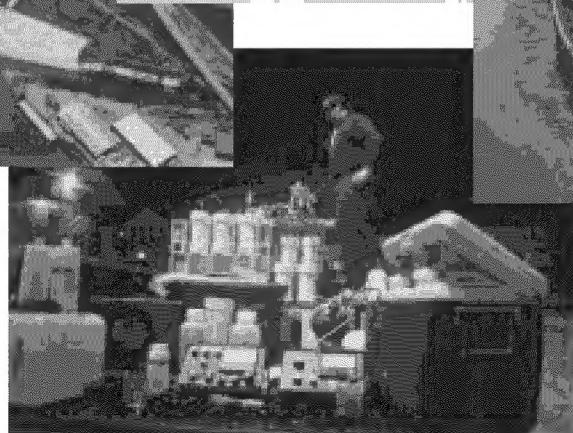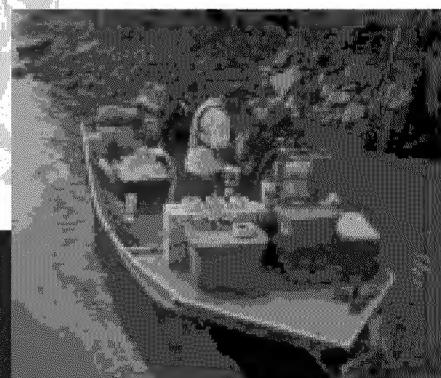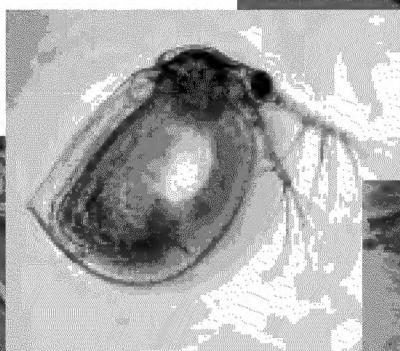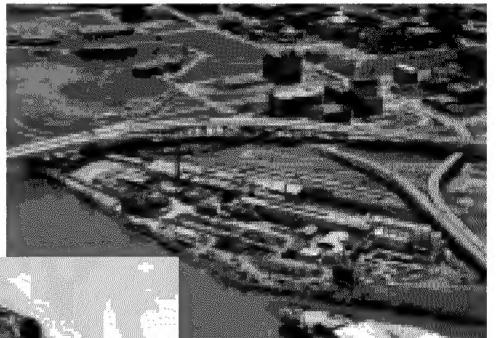
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Cover photographs:

Top: The ASARCO facility in Omaha Nebraska, on the bank of the Missouri River, lies mostly between the Burt-Izard Drain to the north (bottom right of the picture) and Interstate 80 to the south. Photo taken April 1992 by Aerpic-Camera, Omaha, NE 68104.
Right: Sediment porewater extraction on site on the Missouri River in a USGS boat.
         Photo by John Delashmit, USEPA
Bottom: Porewater extraction during the night. Extraction was completed within 12 hours of field collection of sediment. Photo by Steve Olson, USGS Columbia Environmental Research Center
Center: Adult female *Ceriodaphnia dubia*, the toxicity test organism used in this study.
         Photo by Robin Calfee, USGS Columbia Environmental Research Center.
Left: May 2001 photo of the ASARCO site, showing ongoing conversion to a city park. Aerpic-Camera, Omaha, NE 68104.

Toxicity and Bioavailability of Metals in the Missouri River Adjacent to a Metal Refinery

By

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and
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Toxicity and Bioavailability of Metals in the Missouri River adjacent to a Lead Refinery

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Abstract. This study is an evaluation of the potential environmental impacts of contaminated groundwater from the ASARCO metals refining facility adjacent to the Missouri River in Omaha, Nebraska. Surface waters, sediments, and sediment pore waters were collected from the Burt-Izard drain, which transects the facility, and from the Missouri River adjacent to the facility. Groundwater was also collected from the facility. Waters and sediments were analyzed for inorganic contaminants, and the toxicity of the waters was evaluated with the *Ceriodaphnia dubia* 7-day test. Concentrations of several elemental contaminants were highly elevated in the groundwater, but not in river sediment pore waters. Lead concentrations were moderately elevated in whole sediment at one site, but lead concentrations in pore waters were low due to apparent sequestration by acid-volatile sulfides. The groundwater sample was highly toxic to *C. dubia*, causing 100% mortality. Even at the lowest groundwater concentration tested (6.25%) *C. dubia* survival was reduced; however, at that concentration, reproduction was not significantly different from upstream porewater reference samples. Sediment pore waters were not toxic, except reproduction in pore water collected from one downstream site was somewhat reduced. The decrease in reproduction could not be attributed to measured elemental contaminants.

Key words: Acid-volatile sulfides, arsenic, ASARCO, AVS, brownfields, cadmium, Omaha City (Neb.), sediment pore water, SEM

Introduction

The American Smelting and Refining Company (ASARCO) Omaha facility, located at 500 Douglas Street in Omaha, Nebraska, was a primary lead refinery designed and operated to process lead bullion containing recoverable amounts of several different metals. Refinement was achieved using traditional pyro-metallurgical processes including addition of metallic and non-metallic compounds to molten lead to remove impurities. The Omaha plant produced refined lead and specialty metal by-products including antimony-rich lead, bismuth, dore (silver-rich material) and antimony oxide. The 23-acre facility, which lies along the Missouri River, was closed in July 1997. Remediation at the facility is being addressed under the state Remedial Action Plan Monitoring Act (RAPMA), a voluntary remediation program. Numerous buildings and structures remain on the site. The approved remediation plan calls for complete demolition of all site structures, regrading, and capping of the site.

Previous characterization and remedial design documents submitted by ASARCO on behalf of the Omaha plant have failed to clearly define the level of threat that previous releases and contaminated groundwater underlying the facility poses to biota living in the adjacent Missouri River. The potential threat stems from elevated levels of arsenic, lead, and other metals in the groundwater. Groundwater elevation data indicate that most of the underlying contaminated groundwater moves into the Missouri River. Lead concentrations in water surface grab samples collected periodically by ASARCO's contractor (Hydrometrics, Inc.) were sometimes higher than those collected immediately upstream from the site. In March 1997, ASARCO collected surface water and sediment samples from the Missouri River and a small on-site tributary (known as the Burt-Izard sewer outfall) and obtained analytical results. Elevated levels of inorganic contaminants in some river sediments have also been reported by Hydrometrics, Inc. Subsequent to this activity the Nebraska Department of Environmental Quality (NDEQ) made a final decision on the remedial plan for this site. The remedial plan does not specifically address groundwater or river sediments. The U.S. Environmental Protection Agency (USEPA) felt that further investigation of the elevated metal levels in the river sediments near the ASARCO refinery was warranted.

The USEPA entered into an agreement with the US Geological Survey, Biological Resources Division, Columbia Environmental Research Center (CERC) to perform this investigation. Specific objectives of this study were to determine the concentration, bioavailability, and toxicity of metals in the Missouri River adjacent to the site. In this report we present and discuss the findings of this investigation.

Methods

Porewater toxicity testing

A porewater approach was undertaken to determine the bioavailability and toxicity of metals at the site. For many inorganic contaminants, ecological risk is associated with the free metal ion concentration in water. Pore water is the interstitial water between sediment particles. Because of restricted mixing within sediments, pore waters are in contact with sediments for a long time relative to surface waters. Consequently, porewater concentrations of sediment-associated contaminants are often elevated relative to overlying waters, and may represent a worst-case scenario in terms of ecological risk to aquatic organisms in overlying waters.

Because contaminants may be associated with sediments through a number of different mechanisms, not all sediment-associated contaminants are available for dissociation into pore waters--i.e., not all are equally bioavailable. For inorganic contaminants (metals and metalloids), such associations may be very loose, such as would be represented by electrochemical attraction to the charged surfaces of clay mineral particles. These contaminants can be dislodged by changes in ionic composition or concentration of the surrounding water. On the other end of the availability spectrum are those elements of concern that may be part of the mineral phase itself. The metal sulfides--the ores refined at the ASARCO facility-- represent this condition. These metals are only released to the liquid phase upon complete destruction of the mineral matrix (i.e., by digestion with strong acids) and are not generally considered to be biologically available (Tessier et al. 1979; Gobas and Zhang 1994). Intermediate associations between elemental contaminants and sediment particles include sorption and other interactions with iron and manganese hydroxides; and complexation by sediment organic matter, including the humic and fulvic acids.

The analysis of bulk sediments for total metals generally involves the complete digestion of the matrix. Consequently, this method may include the measurement of metals and other elements that are not biologically available, and when used alone may

overestimate ecological risk. We therefore also incorporated a method of dissociation (leaching sediments with a weak acid, 1-N HCl) that simulates relevant biological conditions (DiToro et al. 1992) for assessing and evaluating the biological availability of sediment-associated contaminants at the ASARCO-Omaha facility and adjacent areas of the Missouri River. We considered this method, which does not consider those metals bound to acid-volatile sulfides as bioavailable (DiToro et al. 1992), to be the most appropriate for assessing sediment-associated contaminants at the ASARCO facility. In addition, contaminated ground water seeping into the river from beneath the ASARCO facility would first

intersect the sediment pore water, which makes assessment of pore water highly appropriate for this study. Use of the porewater technique also allows testing with the Cladoceran *Ceriodaphnia dubia*, which is highly sensitive to metals but not to ammonia. The latter is a likely contaminant in urban environments that can confound test results with ammonia-sensitive organisms. The use of the porewater medium also eliminates the problem of grain size preference by the test organisms, which sometimes confounds whole-sediment toxicity tests.

Site selection

Figure 1 represents a map of the site and the sampling locations. During a site visit in the spring of 1998,
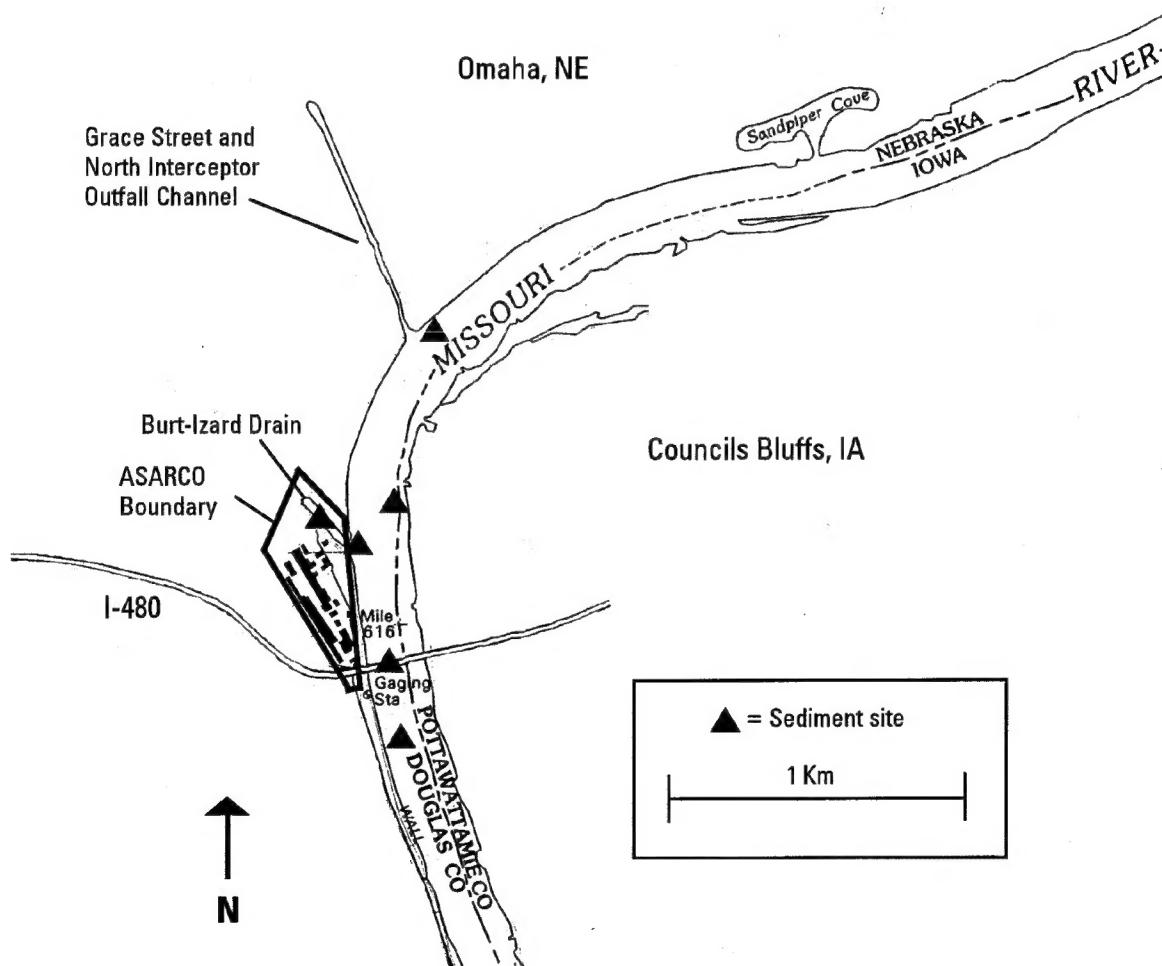

Figure 1. Location of sediment sampling sites near the ASARCO facility in Omaha, Nebraska. Site 1 is the site farthest north. Site 2 is on the eastern bank. Site 4 is within the Burt-Izard Drain, and Site 5 is in the Missouri River at the mouth of the Burt-Izard. Site 24 is under the I-480 Bridge and Site 25 is the farthest south. Approximate boundary of ASARCO facility is indicated.

sandy sediments were found along the ASARCO waterfront. It was also determined that there were three likely paths of groundwater movement from the ASARCO facility into the river: 1) general seepage along the waterfront, 2) the Burt-Izard Drain, an open ditch running along the northern boundary of the site, and 3) the Chicago Street Drain, a now perforated storm drain traversing the property at a depth of about 2 m below the ground surface. Therefore, it was determined that sediment would be taken from one site within the Burt-Izard Drain (which is an open ditch or creek) and one at its confluence with the river. Two sites were to be sampled at the mouth of the Chicago Street Drain (which is a pipe buried at approximately 4 m depth). In addition, two sediment samples were to be taken just upstream of the ASARCO facility, one on the same (west) bank and one just upstream of the ASARCO facility on the opposite (east) bank. The upstream sediment sites were to function as reference sites. Sites along the waterfront of the facility were also selected for sediment sampling. At the time of sampling nearly all of the sediment had been scoured from this outside-bend area. Consequently, sediment was collected as planned from the site within the Burt-Izard Drain (Site 4) and at its mouth (Site 5), and from the reference site across the river (Site 2). However, there was no sediment to sample anywhere along the ASARCO waterfront. The sandy sediments that had been observed there in the spring had been removed by subsequent high water. The bottom along this outside bend of the Missouri River consisted primarily of riprap and slag. A search for an appropriate upstream same-side-of-river sediment sample was only successful after moving approximately 0.75 kilometers upstream. This sample (Site 1) was collected from an eddy upstream of the outfall channel for Grace Street and North Interceptor. Sediment was found in two eddy areas downstream from the plant and these were sampled (Site 24 and Site 25). It was decided at the time of sampling that sites further downstream would be highly complicated by other potential inputs, and no further sediment sampling was conducted.

A sample from one of the monitoring wells near the river (MW19) was provided by ASARCO, which we analyzed and tested to determine the potential toxicity of ground water entering the river. In addition, two surface water samples were taken from the Missouri River. The river water samples served as additional references to verify that *C. dubia* was in fact adaptable to the water quality of the river and to verify that no upstream toxic releases occurred on that date that might confound the test.

Field procedures

Sediment was collected on October 5, 1998. A Ponar dredge was used to sample sites over a meter deep, which includes all sites except Site 4. A 10-cm diameter coring device (Onuf et al. 1996) was used at Site 4. A Rockwell® PLGR global positioning system was used to record the position of sampling sites.

Pore water was extracted on site by means of pressure filtration using an apparatus similar to that described in Carr and Chapman (1995) and retained in an acid-washed polyethylene sample bottle. Nitrogen gas (analytical grade) was used as the source of pressure, and pressure in the extraction devices did not exceed 35 psi. Not all porewater extraction was completed before leaving the site, but extractions were completed within twelve hours of sample collection. Between two and three liters of pore water were collected at each site. Surface water samples were collected by completely submersing the sample bottle, opening the lid and filling the bottle, and then recapping the bottle underwater.

Conductivity, pH, and dissolved oxygen were measured on each aqueous sample immediately after collection. Dissolved oxygen was determined with a YSI® model 57 dissolved oxygen meter and conductivity was determined using a YSI® S-C-T meter. Orion® 290A meters with a glass gel electrode were used to measure pH. An 100 mL aliquot of each aqueous sample (pore, surface, or ground water) was filtered with a 0.45 µm polycarbonate filter and acidified with 1% ultrapure nitric acid (v:v) for metals preservation. Two filtration blanks were also prepared using reverse osmosis water and preserved. One of these was collected before on-site filtration began and the other as the last filtration of the batch. Two aliquots of the sediment from which each pore water was extracted were also retained for metals analysis. All equipment that contacted sediment or sediment pore water was acid-washed prior to use. All aqueous samples to be used in toxicity tests were centrifuged (3000 g for 10 minutes) to remove fines after arrival at CERC. All samples, aqueous or solid-phase, were kept on ice or refrigerated (T=5°C) until use.

Laboratory procedures

Rearing of test organisms

Based on data provided by Hydrometrics, Inc, it was determined that Missouri River water from the Omaha area is usually somewhat higher in potassium, sodium and sulfates than the CERC well water in which our test organisms are normally reared. Therefore, *C. dubia* were reared at the CERC for more than three months prior to the tests in a reconstituted water formulated to approximate that of the river. Reconstituted river water was made by addition of 180 mg of K_2SO_4 and 1980 mg of Na_2SO_4 to 15L of CERC well water. The water chemistry of this reconstituted water is given in Table 1. New reconstituted river water was made weekly and allowed to mix and aerate overnight before use. Culture techniques were similar to those described in USEPA (1994). *Ceriodaphnia* were fed a diet of fermented trout chow, yeast, and cereal leaves (YTC; USEPA 1994) and algae (*Selenastrum capricornutum* and *Ankistrodesmus falcatus*; 60:40 mix).

Table 1. Comparison of historical river water chemistry, Columbia Environmental Research Center (CERC) well water, and reconstituted river water. Historical averages of river water chemistry computed from unpublished Hydrometrics, Inc. data, and supplied to CERC by USEPA. All values in mg/L.

Element	Historical average	CERC well	Reconstituted river water
Sodium	66.5	23.0	66.0
Potassium	7.9	2.2	7.9
Calcium	67.7	71.0	71.0
Magnesium	25.4	27.0	27.0
Chloride	17.1	21.0	21.0
Bicarbonate	184	188	188
Sulfate	212	47.0	145
Summation of identified salts	580	379	526

Toxicity tests

Toxicity tests were performed using the *C. dubia* 7-day survival and reproduction test (USEPA 1994). USEPA (1994) stipulates the use of a dilution series for effluent toxicity testing, but not normally for environmental samples collected outside the mixing zone. We tested a dilution series of the groundwater sample (100, 50, 25, 12.5, and 6.25%) to determine the degree of toxicity of this water in the *C. dubia* test. We also tested a dilution series (100, 50, and 25%) of the pore water collected from within the Burt-Izard drain. Reconstituted river water was used as the diluent.

The hardness and alkalinity of surface water samples and some porewater samples were higher than expected, ranging from 250 mg/L to over 700 mg/L hardness as $CaCO_3$. Therefore, another reconstituted water, designed to reflect the chemistry of the surface waters collected on October 5, was also prepared from CERC well water and salts. This "Hard Recon" was tested as an additional treatment, to verify that *C. dubia* were tolerant of this very hard, alkaline, high-sulfate water. To make this second reconstituted water, 236 mg of $CaSO_4$, 34.8 mg of $MgSO_4$, and 129 mg $NaHCO_3$ were added per each liter of well water. Well water chemistry is described in Table 1.

A positive control dilution series (i.e., reference toxicant) consisting of three concentrations of NaCl in CERC well water (2.50, 1.25, and 0.613 parts per thousand) was also tested concurrently with the toxicity test. Lastly, a procedural control in CERC well water was also performed concurrently with the test. *C. dubia* used in the well water control were reared in well water instead of reconstituted river water.

The *C. dubia* toxicity tests were conducted according to USEPA (1994). Animals were exposed to 15 mL of the sample or the appropriate dilution in 30-mL glass beakers for seven days. One neonate, less than 12 hours old, was added to each beaker at the beginning of the test (day 0). There were ten replicates of each treatment. Waters were renewed daily. Endpoints, recorded daily, were lethality (absence of movement) and reproduction (number of neonates produced). Temperature in the test beakers was maintained at 25± 1°C by means of a temperature-controlled water bath. Test organisms were fed 1 mL of YTC and 1 mL of algae after renewal.

Sediment and water quality measurements

Hardness, alkalinity, dissolved oxygen, pH, conductivity, nitrate+nitrite, sulfate, phosphate, chloride, calcium, and ammonia concentration of aqueous samples were measured after arrival at CERC. Hardness, alkalinity, calcium, and chloride were determined by titration. Dissolved oxygen was determined with a YSI® model 57 dissolved oxygen meter and conductivity was determined using a YSI® S-C-T meter. Orion® EA 940 meters with glass gel electrodes were used to measure pH. The Orion EA940 meters with an Orion® Model 95-12 ammonia ion selective electrode were employed for ammonia determinations. Sulfate, nitrate+nitrite, and phosphate concentrations were measured with a Hach® DR 2000 spectrophotometer. Dissolved organic carbon of sediment pore water was measured with a Technicon AAII® system. Sediment grain size was determined with the Bouyoucous Hydrometer Method. Standard operating procedures for these techniques can be found in USEPA and USGS (1998).

Daily during the test, water from exposure beakers (post-exposure) was collected for dissolved oxygen, pH and conductivity measurements. Hardness, alkalinity, and ammonia concentrations were also measured in the post-exposure water on day 4 and day 7. In order to have sufficient volume of post-exposure sample, water from all replicates within a treatment was composited in a 250-mL beaker for these analyses.

Sample preparation and analysis

Water: No further chemical preparation was conducted on acidified water samples prior to analysis. Samples were first subjected to a semiquantitative scan by inductively coupled plasma-mass spectrometry (ICP-MS) to indicate concentrations of target and other elements of interest, to reveal the presence of unexpected elements, to determine optimal dilutions for quantitative analysis, and to identify samples appropriate for QC purposes in the quantitative run.

The semiquantitative scan is reported to be $\pm30\%$ to $\pm50\%$ in accuracy by the manufacturer. In addition, all water samples were subjected to an ICP-MS quantitative analysis which targeted the main elements of interest (Zn, As, Cd, and Pb). In this analysis, Pb was monitored and reported as the sum of three isotopes (Pb-206 + Pb-207 + Pb-208). Two masses were monitored for Zn and Cd, but only one reported (Zn-66 and Cd-114).

Sediment AVS and SEM: For AVS and SEM determination, each sediment sample was briefly homogenized in its collection container with a plastic scoop, following which a ~5 mL aliquant was taken for AVS determination. During the AVS determination on each sediment sample, a simultaneously extractable metals fraction was generated in 1N hydrochloric acid. Fifty mL of each extract was vacuum filtered through a 0.4 µm polycarbonate membrane. A silver/sulfide electrode was used for determining AVS (Brumbaugh et al. 1994; Brumbaugh and Arms 1996). For determination of Zn, As, Cd, and Pb by quantitative analysis ICP-MS, a portion of each filtered SEM extract (10 mL) was subjected to a microwave oven nitric acid/hydrogen peroxide digestion to minimize potential interference from Cl⁻ during analysis. Final dilution volume for the digestates was 50 mL in a matrix of 2% nitric acid. The resulting digestates were analyzed by quantitative ICP-MS as described above for water (May et al. 1997).

Sediment Total Recoverable Metals: A portion of each sediment sample was lyophilized and then homogenized to a coarse powder, following which a dried aliquant was digested in a sealed Teflon vessel in a microwave oven with nitric acid, hydrochloric acid, and hydrogen peroxide to prepare a digestate suitable for quantitative and semiquantitative scan by ICP-MS as described above for water. Final acid matrix was 5% nitric acid and 0.5% HCl.

Quality Control: Extensive quality control was conducted as part of preparation and analysis of samples. Where samples were subjected to a digestion (i.e., sediment), quality control included digestion blanks, sample replicates, spikes, and reference materials. Quality control for quantitative ICP-MS (all samples) included duplicate analyses, dilution checks, reference solutions, analysis spikes, an interference check, and calibration checks. For the semiquantitative scan, the following quality control was included: a calibration check, an analysis spike, and a precision check. As part of the quality assurance procedures, CERC also analyzed "blind" water and sediment samples provided by USEPA.

Details of preparation and analytical protocols and quality control results can be found in CERC reports FY-99-32-03 and FY 99-32-04.

Statistical analysis

Survival data were evaluated with logistic analysis (Agresti 1990). Analysis of variance with rank transformation (Snedecor and Cochran 1989) was used to evaluate reproduction data. In the analysis of variance, total reproduction for each daphnid over the seven-day test (including those that died during the experiment) was the dependent variable. Experimentwise error rates for all pairwise comparisons were controlled at $\alpha = 0.05$ with Tukey's method (Hochberg and Tamhane 1987).

The influence of metal concentrations on survival and reproduction was assessed with principal components analysis (Johnson and Wichern 1992). Principal components analysis was performed to find relationships between measured water quality and metals variables and the toxicity test data. Duplicate field water samples were taken at Site 1 and an average of the resulting element concentrations was used to represent that site. Elements with at least half the observations above detection limit were included in the analysis. In addition, Br was excluded from the sediment database since it had identical concentrations at each site where it was measured. Detection limit / 2 was used for analysis when a concentration was recorded as below detection limit. Concentration data from water samples from MW19 was excluded from analysis since concentrations found there were so high in relation to other sites that they unduly influenced the entire analysis. Concentrations were log transformed prior to analysis using the formula $\log_{10}(x+1)$. Thirty-nine elements from sediment samples were retained for analysis, including: Al, As, Ba, Ca, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ho, K, La, Li, Mg, Mn, Mo, Na, Nd, Ni, Pb, Pr, Rb, Sb, Sm, Sn, Sr, Tb, Ti, V, Y, Yb, Zn, and Zr. Thirty-one elements from water samples were retained for analysis, including: Al, As, B, Ba, Br, Ca, Cd, Ce, Co, Cr, Cu, Fe, Ga, I, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Sn, Sr, Ti, U, V, W, and Zn.

In addition, a hierarchical cluster analysis was performed to evaluate similarity between sites in terms of elemental composition of water and sediment samples (Kaufman and Rousseeuw 1990).

Results and Discussion

Site locations

It was difficult to find sediment near the ASARCO facility. During the spring site visit, we had determined that we would not sample below the I-480 bridge, just downstream of the ASARCO facility, because there was a large storm drain at that site that could confound the results. Because there were no sediments directly adjacent to the ASARCO facility, we were forced to forego that decision and collect sediments at alternate locations. However, it should be noted that at the time of sample collection, no water was entering the river through these drains, despite the heavy rain that had occurred during the previous night. These drains are very likely non-functional. Sites 2 (reference site across the river), 4 (upstream on the Burt-Izard Drain) and 5 (mouth of the Burt-Izard Drain) were the only planned sites at which we were able to collect sediments. Site1 was moved approximately 0.75 kilometers upstream (above the confluence of the Grace Street and North Interceptor drain). Sites 24 and 25 were added in order to have sediments collected downstream of the facility. Site 24 was collected directly under the I-480 bridge, and Site 25 was collected from an eddy 150 m downstream of the bridge. Figure 1 indicates the locations of the revised sediment sampling sites.

Water quality and sediment description

Field measurements of dissolved oxygen, conductivity and pH and initial measurements of these parameters at the laboratory are given in Table 2. Dissolved oxygen concentrations of pore water and groundwater increased between collection in the field and arrival at the lab. The pH values also increased slightly. Table 3 contains additional water quality measurements measured at CERC that were not also measured in the field.

Table 2. Comparison of dissolved oxygen concentrations, conductivity, and pH measurements performed in the field with measurements made at CERC before the start of the toxicity test, including measurements on CERC reference waters and on dilutions of sample waters. MW19 is the groundwater sample from monitoring well 19. SEDx refers to pore waters collected from the various sediment sites. NaCl refers to the sodium chloride reference toxicant treatments and the concentration of NaCl added to reconstituted river water. Hard Recon refers to the reconstituted water made to reflect the water quality of the river waters.

	Field Measurements			Measurements at CERC		
	Dissolved Oxygen (mg/L)	Cond. (μmhos/cm^2)	pH	Dissolved Oxygen (mg/L)	Cond. (μmhos/cm^2)	pH
River water 1	8.3	600	8.83	9.5	600	8.34
River water 2	9.1	600	8.02	9.7	610	8.33
SED 1	4.2	690	7.34	10.2	810	7.75
SED 2	4.6	800	7.62	9.6	790	8.07
SED 4-100%	3.2	600	7.58	9.4	610	7.92
SED 4-50%				9.6	575	8.14
SED 4-25%				9.6	510	8.17
SED 4-12.5%				9.4	500	8.18
SED 5	5.8	800	6.99	10.2	1310	7.61
SED 24	7.9	580	7.58	9.6	710	8.30
SED 25	5.3	650	7.73	10.2	900	7.88
MW19-100%	3.8	2980	7.42	10.2	3110	8.25
MW19-50%				9.8	1400	7.98
MW19-25%				9.6	1200	8.08
MW19-12.5%				9.6	850	8.15
MW19-6.25%				9.6	690	8.16
NaCl 2.5%				8.5	4620	8.19
NaCl 1.25%				8.5	2600	8.19
NaCl 0.613%				8.8	1510	8.19
Reconstituted river water				8.6	510	8.17
Hard Recon				8.0	580	8.26
CERC well water				8.6	341	8.48

Table 3. Water quality measurements taken before start of *Ceriodaphnia* toxicity test. MW 19 is the groundwater sample from monitoring well 19. SEDx refers to pore waters collected from the various sediment sites. NaCl refers to the sodium chloride reference toxicant treatments and the concentration of NaCl added to reconstituted river water. Hard Recon refers to the reconstituted water made to reflect the water quality of the river waters. Units are mg/L.

	DOC	Alkal. (as $CaCO_3$)	Hard. (as $CaCO_3$)	NH_3 (as N)	NO_{2+} NO_3	SO_4	PO_4	Cl	Ca
River water 1	3.3	162	244	0.068	0.52	182	0.109	8.8	71.8
River water 2	7.9	162	244	0.070	0.50	171	0.133	13.8	79.8
SED 1		390	416	2.07	0.00	131	0.830	8.8	112
SED 2	8.2	344	390	0.965	0.29	162	0.149	13.8	112
SED 4	1.2	160	208	11.2	0.40	120	0.316	13.8	87.9
SED 5	15.2	776	748	13.5	0.00	103	0.257	8.8	193
SED 24	4.6	234	336	0.547	0.44	161	0.162	13.8	96.0
SED 25	6.6	366	410	1.47	0.25	143	0.167	23.9	128
MW 19	6.5	402	550	1.20	0.15	186	0.806	321	185
Reconstituted river water		250	228	0.0201	0.60	74.0	0.066	8.8	169
Hard Recon		240	250		0.68	154	0.042		
Well	1.2	246	284	0.027	0.40	63.6	0.060	13.8	39.5

Table 4 gives the grain size analysis of the sediments. Sites 4 and 5, collected from opposite ends of the Burt-Izard drain, were very different from the other samples. Site 4 was alone in having a high percentage of particles larger than sand size, almost a third by weight. The remainder of Site 4 sediment was composed almost entirely of sand. Site 4 also had the lowest moisture content and the lowest organic content, as determined by loss on ignition (LOI). Despite its proximity to Site 4, Site 5 differed to the other extreme, being the lowest in sand (26%), and highest in silt (52%) and clay (21%). Site 5 was also the highest in moisture and more than double any other site in organic content (as indicated by LOI). Site 4 was located within the Burt-Izard Drain, and probably received high runoff flows during rain events, which would explain the large grain size and the presence of many particles of glass and what appeared to be road debris. Site 5 was located in a low velocity eddy at the mouth of the Burt-Izard, which explains its different texture and consistency.

Table 4. Results of grain size analysis of sediments collected in the Missouri River and in the Burt-Izard Drain, near ASARCO facility, Omaha, Nebraska. Percentages of sand, silt and clay determined by the Bouyoucous hydrometer method, larger particles separated by sieving.

Sample designation	Percent larger than sand	Sand %	Silt %	Clay %	Percent Moisture	Percent Loss on Ignition
SED 1	0.0	47.5	42.0	10.5	28	1.4
SED 2	0.0	63.0	29.0	8.0	27.8	1.5
SED 4	32.0	66.0	1.0	1.0	18.2	0.80
SED 5	0.0	26.3	52.0	21.8	41.8	3.7
SED 24	0.0	86.5	10.5	3.0	20.6	0.8
SED 25	1.5	81.3	12.8	4.5	22.1	1.3

The monitoring well groundwater sample differed in many respects from the other water samples. Conductivity of the groundwater sample was nearly 3000 µhos/cm^2, which was five-fold higher than river water (600 µmhos/cm^2). The conductivity of the groundwater sample stems largely from its very high chloride concentration (321 mg/L). In contrast, ammonia, nitrate+nitrite, sulfate, phosphate, and calcium concentrations were not highly elevated in the groundwater sample.

Although some pore waters were low in dissolved oxygen immediately after collection, all samples were well within concentrations acceptable to *C. dubia* before the start of the toxicity test. Some pore waters were high in ammonia (notably Sites 4 and 5) but such concentrations have not been shown to be toxic to *C. dubia* (Monda 1991). Daphnids are much less sensitive to ammonia than fish, while having a high sensitivity to other toxicants, which makes them an ideal organism for sediment porewater testing.

As noted in the introduction, organic material in the environment complexes and/or sorbs some contaminants, which renders them less bioavailable than contaminants less strongly bound to particulates (Tessier et al. 1979; Gobas and Zhang 1994). In all but Site 5, porewater DOC concentrations were in the same range as the surface water samples, which is very low

for pore waters (Table 3). Site 5 porewater DOC concentration was quite high (15.2 mg/L), which is in concordance with the high LOI and fine texture of that sediment (Table 4).

Metals concentrations

The quality control results were considered to be acceptable based on specifications established by CERC. Recovery from the "blind" QA samples provided by EPA was very good. Quantitative analysis results were well within the control limits, and the semiquantitative results were all within 25% of the USEPA value, and most were within 10%.

The results of the quantitative analysis of sediment are found in Table 5, and the quantitative analysis of aqueous samples is found in Table 6. The monitoring well sample (MW19) had strongly elevated concentrations of cadmium, zinc and arsenic, but the lead concentration was not high (Table 6). Site 25 had a somewhat elevated concentration of lead in the whole sediment (39.8 µg/g dry weight; Table 5), however whole sediment concentrations of cadmium, zinc, and arsenic were not remarkable. With the exception of MW19, none of these four elements were found in concentrations above the individual water quality in any aqueous sample.

Table 5. Concentrations (µg/g dry weight) of total recoverable arsenic, cadmium, lead and zinc in sediment samples from the Omaha, NE, ASARCO study. Measurements are from quantitative analysis by ICP-MS.

Element	SED 1	SED 2	SED 4	SED 5	SED 24	SED 25	EPA blind QA sample	MDL[a]
Arsenic	5.60	6.50	2.90	7.80	5.90	6.90	4.60	0.31
Cadmium	< 0.27	< 0.27	< 0.27	0.43	< 0.27	< 0.27	0.78	0.27
Lead	8.40	7.10	7.40	19.7	13.0	39.8	7.00	1.10
Zinc	39.0	34.5	33.7	77.2	23.9	45.8	41.0	5.10

[a] MDL = method detection limit

Table 6. Concentrations (μg/L) of arsenic, cadmium, lead and zinc in aqueous samples from the Omaha, NE, ASARCO study. MW19 is the groundwater sample from monitoring well 19. SEDx refers to pore waters collected from the various sediment sites. NaCl refers to the sodium chloride reference toxicant treatments and the concentration of NaCl added to reconstituted river water. Hard Recon refers to the reconstituted water made to reflect the water quality of the river waters. Measurements are from quantitative analysis by ICP-MS.

Sample identification	Arsenic	Cadmium	Lead	Zinc
Filtration Blank 1	< 0.07	1.00	0.23	8.20
Filtration Blank 2	< 0.07	0.03	0.49	2.60
River Water 1	2.70	0.79	0.50	11.3
River Water 2	2.70	0.52	0.64	4.20
MW19	574	21.5	2.60	1570
SED 1 Pore water	30.7	0.15	3.40	9.8
Dup. SED 1 Pore water	30.4	1.20	5.20	21.9
SED 2 Porewater	15.6	0.67	1.70	27.5
SED 4 Pore water	23.1	0.67	8.40	34.7
SED 5 Pore water	56.3	0.49	2.20	17.2
SED 24 Pore water	4.00	1.10	11.5	63.7
SED 25 Pore water	7.70	0.77	5.00	31.9
USEPA Blind Sample	13.3	18.10	4.90	12.9
MDL[a]	0.07	0.02	0.04	0.42

[a] MDL = method detection limit

Cadmium, zinc, arsenic, and especially lead were identified *a priori* as contaminants of concern at ASARCO-Omaha lead refinery. However, it is possible that unidentified elements (i.e., byproducts of lead refining processes or waste products from the ore-bearing material) could cause toxicity at these sites. Thus, we performed an additional broad-spectrum analysis of 64 elements in pore water, water, and sediment. These analyses were semiquantitative in nature, but have sufficient accuracy to identify most potential elemental contaminants of concern should they be present in toxic concentrations. The results of the semiquantitative sediment analyses are presented in Table 7, and the semiquantitative analysis of aqueous samples is in Table 8. The groundwater from the monitoring well was high in many elements (Table 8). The semiquantitatively measured concentrations of metals in sediments were not remarkable, but verified the somewhat elevated level of lead (40 μg/g) at Site 25 identified in the quantitative analysis.

Table 7. Concentrations (μg/g dry weight) of elements in sediment from the ASARCO facility in Omaha, Nebraska determined by semiquantitative ICP-MS scan.

Element	SED 1	SED 2	SED 4	SED 5	SED 24	SED 25	EPA Blind QA Sample
Ag	< 0.1	< 0.1	0.2	0.2	< 0.1	0.1	0.1
Al	4000	4000	900	7000	3000	3000	6000
As	6.00	7.00	4.0	9	7.0	8.0	5.0
Au	0.3	0.2	0.6	< 0.1	< 0.1	< 0.1	0.8
B	1	2	< 1	2	< 1	< 1	3
Ba	200	200	30	200	400	300	90
Be	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Bi	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Br	10	10	10	10	10	10	10
Ca	13000	14000	45000	16000	11000	12000	88000
Cd	0.6	0.3	0.2	0.6	< 0.1	0.2	0.9
Ce	20	20	10	30	20	20	30
Co	5	6	3	7	4	5	4
Cr	8	9	30	10	7	8	8
Cs	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Cu	9	6	30	20	3	5	8
Dy	2	2	0.6	2	1	1	2
Er	0.7	0.7	0.2	1	0.6	0.6	0.9
Eu	0.5	0.5	0.2	0.6	0.4	0.4	0.6
Fe	7000	8000	11000	10000	6000	7000	7000
Ga	3	3	1	4	2	2	4
Gd	2	2	0.8	3	2	2	3
Ge	< 0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1
Hf	< 0.1	< 0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.1
Ho	0.3	0.3	< 0.1	0.4	0.2	0.2	0.3
I	< 1	< 1	< 1	< 1	< 1	< 1	< 1
In	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Ir	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
K	800	900	200	1000	500	500	600
La	10	10	5	10	10	10	10
Li	5	5	< 1	7	4	4	5
Lu	< 0.1	< 0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.1
Mg	5000	5000	1000	4000	4000	4000	17000

Table 7., continued

Element	SED 1	SED 2	SED 4	SED 5	SED 24	SED 25	EPA Blind QA Sample
Mn	400	400	200	500	200	300	500
Mo	0.4	0.3	9	0.6	0.3	0.3	0.8
Na	100	200	100	200	200	200	100
Nb	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Nd	10	10	4	10	10	10	10
Ni	10	10	30	20	10	10	10
Os	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Pb	10	6	8	20	10	40	6
Pd	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Pr	3	3	1	4	3	3	4
Pt	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Rb	9	9	2	10	4	6	5
Re	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Ru	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Sb	0.2	< 0.1	0.6	0.2	0.4	0.5	0.4
Sm	2	2	0.8	3	2	2	3
Sn	0.1	0.2	3	< 0.1	0.1	0.2	0.2
Sr	50	50	100	70	30	40	200
Ta	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Tb	0.3	0.3	< 0.1	0.4	0.3	0.3	0.4
Te	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Ti	70	80	30	60	90	70	40
Tl	0.1	0.1	< 0.1	0.2	< 0.1	< 0.1	< 0.1
Tm	< 0.1	< 0.1	< 0.1	0.1	< 0.1	< 0.1	0.1
U	< 1	< 1	< 1	< 1	< 1	< 1	< 1
V	10	20	4	20	10	10	10
W	< 0.1	< 0.1	0.5	< 0.1	< 0.1	< 0.1	< 0.1
Y	8	8	2	10	7	7	9
Yb	0.7	0.7	0.2	0.9	0.5	0.5	0.7
Zn	60	50	50	90	30	50	50
Zr	2	3	1	5	2	3	2

Table 8. Concentrations of elements in water from the Omaha, NE, ASARCO study determined by semiquantitative ICP-MS scan. Units are µg/L unless otherwise specified.

Element	River water 1	River water 2	Site 1	Site 1 Dup	Site 2	Site 4	Site 5	Site 24	Site 25	MW 19	Filter Blank 1	Filter Blank 2	EPA QA sample
Ag	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Al	8	<0.1	10	<0.1	<0.1	18	0.5	22	54	39	2	0.84	82
As	4.2	4.0	38.0	39.0	19.0	28.0	72.0	5.6	11	771	0.10	0.15	16.0
B	63	57	51	46	90	95	147	52	223	6520	<1	<1	<1
Ba	63	61	178	177	130	144	335	117	212	166	1	<1	<1
Be	0.25	0.16	<0.1	<0.1	0.15	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	5
Bi	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Br	102	103	199	196	190	121	634	138	184	551	2.8	2.3	1.5
Ca[a]	57	56	90	84	92	54	171	80	88	172	0.11	<0.1	<0.1
Cd	0.92	0.61	0.27	1.3	0.7	0.75	0.55	1	1.1	26	1.2	<0.1	20
Ce	0.17	<0.1	0.31	0.1	0.11	0.63	0.05	0.19	0.12	<0.1	<0.1	<0.1	<0.1
Co	0.17	0.11	2.2	2.3	1.4	1.2	4.2	0.86	1.5	11	<0.1	<0.1	47
Cr	3.1	5.2	11	16	7.6	5.6	24	9.2	17	16	0.75	0.44	7.8
Cs	<1	<1	<1	<1	<1	<1	<1	<1	<1	2.4	<1	<1	<1
Cu	3.2	4.4	3	3.3	4.4	7.9	3	13	4.6	20	3.9	0.61	5
Dy	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Er	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Eu	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Fe	127	71	1520	1320	40	742	4210	238	318	289	17	17	34
Ga	<0.1	<0.1	0.22	0.25	0.17	0.13	0.33	0.11	0.13	0.23	<0.1	<0.1	<0.1
Gd	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ge	<0.1	<0.1	0.23	0.28	<0.1	0.17	<0.1	<0.1	<0.1	0.27	<0.1	<0.1	<0.1
Hf	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ho	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
I	1.7	1.8	15	28	28	4	56	11	11	5.8	<1	<1	<1
In	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Ir	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
K[a]	5.4	5.7	5.1	5.6	6.3	6.5	8.4	5.1	7	92	<0.1	<0.1	<0.1
La	0.11	<0.1	0.18	<0.1	<0.1	0.36	<0.1	0.11	<0.1	<0.1	<0.1	<0.1	<0.1
Li	45	46	35	34	48	29	17	40	40	92	<1	<1	<1
Lu	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Mg[a]	23	22	38	36	37	15	67	32	36	34	<0.1	<0.1	<0.1

[a]Concentration units µg/mL

Table 8., continued

Element	River water 1	River water 2	Site 1	Site 1 Dup	Site 2	Site 4	Site 5	Site 24	Site 25	MW 19	Filter Blank 1	Filter Blank 2	EPA QA sample
Mn	17	5	4970	4630	2800	608	6820	1040	2160	2660	4.9	1.1	52
Mo	3.2	3.3	5.1	5.4	4.8	14	6.8	7.8	10	56	0.2	<0.1	<0.1
Na[a]	67	72	69	68	77	60	94	65	87	532	<0.1	<0.1	<0.1
Nb	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Nd	<0.1	<0.1	0.14	<0.1	<0.1	0.29	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ni	3.7	2.2	7.2	19	6.2	4.7	10	8.9	19	14	2.7	0.36	34
Os	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pb	<1	<1	3.7	5.6	1.8	9.2	2.8	12	5.8	3	<1	<1	5.4
Pd	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pr	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pt	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Rb	2.3	2.3	3.1	3	4.4	3	3	2.7	3.3	134	<0.1	<0.1	<0.1
Re	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.78	<0.1	<0.1	<0.1
Ru	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Sb	0.64	1	0.84	0.78	2.4	8.2	1	4	12	430	0.1	<0.1	<0.1
Sm	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sn	<0.1	0.47	0.38	0.51	0.54	0.93	0.53	0.58	0.4	1.4	<0.1	<0.1	<0.1
Sr	472	522	734	739	798	412	1172	639	752	1230	<1	<1	<1
Ta	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Tb	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Te	<0.1	<0.1	0.16	<0.1	<0.1	<0.1	0.14	<0.1	<0.1	0.24	<0.1	<0.1	<0.1
Ti	1.4	0.62	2.3	1.7	1.2	1.7	2.9	1.8	4.9	8.3	<0.1	0.14	<0.1
Tl	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.69	<0.1	<0.1	<0.1
Tm	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
U	4.2	4.4	2.8	2.8	6.2	4.1	<1	5.5	7.4	5.6	<1	<1	<1
V	2.4	2.3	1.6	1.4	1.6	1.8	0.68	2.8	3.2	2.2	<0.1	<0.1	25
W	0.14	0.13	0.16	0.17	0.26	0.44	0.13	0.11	0.32	13	<0.1	<0.1	<0.1
Y	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Yb	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Zn	21	<1	6.3	22	26	37	21	67	44	2050	12	4	22
Zr	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1

[a] Concentration units $\mu g/mL$

The USEPA chronic criteria for selected metals in water are found in Table 9. Many of the criteria are dependent on water hardness. Table 10 contains the criteria for the sediment pore waters, calculated using the measured hardness values. None of the sediment pore waters exceeded the USEPA water quality criteria of the quantitatively measured metals.

Table 9. USEPA Water Quality Criteria for selected trace metals or the hardness-based algorithms used to determine the criteria [taken from Wildhaber and Schmitt (1996) and USEPA (1999)].

Element	USEPA Chronic criteria (μg/L)
Arsenic	190
Cadmium	$e^{(0.7852[\ln(hardness)]-3.490}$
Copper	$e^{(0.8545[\ln(hardness)]-1.702}$
Lead	$e^{(1.2730[\ln(hardness)]-4.705}$
Nickel	$e^{(0.8460[\ln(hardness)]-1.1645}$
Zinc	$e^{(0.8473[\ln(hardness)]+0.7614}$

Table 10. Calculated USEPA Water Quality Criteria Values for pore waters, river waters, and groundwater based on averaged measured hardness for selected metals. MW19 is groundwater from monitoring well 19, located on the ASARCO Omaha property. SEDx refers to pore waters collected from the various sites. All values in μg/L.

Site	Hardness (mg/L CaCO$_3$)	Cu	Cd	Pb	Ni	Zn
MW19	550	39.9	4.3	27.9	666.9	449.3
River water 1	262	21.2	2.4	10.8	356.1	239.7
River water 2	280	22.4	2.5	11.8	376.7	253.6
SED1	384	29.4	3.3	17.6	492	331
SED2	333	26.0	2.9	14.7	436	294
SED4	242	19.8	2.3	9.8	333	224
SED5	540	39.3	4.3	27.2	657	442
SED24	324	25.4	2.9	14.2	426	287
SED25	369	28.4	3.2	16.8	476	320

The high concentration of lead in Site 25 sediment was not strongly reflected in the pore water, likely because of acid-volatile sulfide (AVS) concentrations in Site 25 sediment. Lead and certain other metals, measured as simultaneously extractable metals (SEM), are not biologically available when bound to AVS (Di Toro et al. 1992). One mole of AVS has the capacity to bind one mole of SEM. For a given total or SEM metal concentration, as the ratio of SEM to AVS becomes greater than one, a sharp increase in porewater metals is expected to follow, providing there is a moderate or high concentration of metal in the sediment (a SEM/AVS ratio greater than one can be inconsequential if both the AVS and SEM concentrations are very low). Concentrations of SEM may be found in Table 11, and a comparison of AVS and SEM concentrations can be found in Table 12. If the summation of the molar concentration of SEM minus the AVS concentration (bottom row, Table 11) is greater than one, then metals exceed the capacity for AVS sequestration and are assumed to be bioavailable.

Table 11. Concentrations of simultaneously extracted metals (µg/g) in sediments collected in the vicinity of the ASARCO lead refining facility in Omaha, Nebraska.

Element	Site 1	Site 2	Site 4	Site 5	Site 24	Site 25	MDL[a]
Arsenic	1.70	2.20	0.48	1.80	1.80	2.30	0.020
Cadmium	0.18	0.20	0.17	0.35	0.099	0.19	0.010
Copper	3.00	2.90	3.50	5.90	1.10	3.30	0.010
Lead	6.60	3.80	26.10	38.30	9.20	43.2	0.030
Nickel	3.60	3.60	3.00	6.50	1.90	3.10	0.020
Zinc	9.70	6.90	79.80	40.80	5.80	23.80	0.490

[a] MDL= Method detection limit

Table 12. Molar concentrations (µmol/g) of acid-volatile sulfide (AVS) and simultaneously extracted metals (SEM) in sediments collected in the vicinity of the ASARCO lead refining facility in Omaha, Nebraska.

Element	Site 1	Site 2	Site 4	Site 5	Site 24	Site 25
AVS	1.60	0.095	8.40	5.00	0.015	1.30
Arsenic	0.023	0.029	0.006	0.024	0.024	0.031
Cadmium	0.002	0.002	0.002	0.003	0.001	0.002
Copper	0.047	0.046	0.055	0.093	0.017	0.052
Lead	0.032	0.018	0.126	0.185	0.044	0.209
Nickel	0.061	0.061	0.051	0.111	0.032	0.053
Zinc	0.148	0.106	1.221	0.624	0.089	0.364
ΣSEM	0.313	0.262	1.461	1.04	0.207	0.711
ΣSEM- AVS	-1.287	0.167	-6.939	-3.96	0.192	-0.589

At equilibrium, different metals are selectively bound by AVS, depending on the solubility of the metal sulfide (Wildhaber and Schmitt 1996). Among the metals and metalloids of concern, mercury is the most strongly bound, followed in order by silver, copper, cadmium, lead, zinc, nickel, arsenic, iron, manganese, and chromium. Therefore, for example, a high concentration of copper could bind all available AVS, leaving none to bind cadmium, lead or other metals less strongly bound by AVS. Wildhaber and Schmitt (1996) used AVS to estimate the porewater concentrations of metals, under the assumption that AVS limits the solubility of these elements. In our study, we did not measure simultaneously extractable mercury or silver. However, the molar concentration of these elements is likely to be low based on extant information, and mercuric and silver sulfides are usually not dissolved by SEM extraction. We therefore ignored these elements in our estimation of SEM binding by AVS.

USEPA water quality criteria (and risk assessment in general) evaluate contaminants individually--not in combination, as they often occur in the environment. To evaluate complex mixtures in sediments, Wildhaber and Schmitt (1996) expanded upon the concept of "toxic units" first proposed by Sprague and Ramsay (1965). A toxic unit is one multiple of the metal's USEPA water chronic criteria concentration in pore water. Because the toxicity of metals is often additive, the summation of the toxic units (STU) for each metal accounts for the cumulative toxicity of the mixture after all its components are scaled for toxicity. Therefore, if the summed toxic units for all metals in a pore water (measured or estimated) is one or greater, the sediment is assumed to be potentially toxic. The estimated toxic units of the sediment pore waters, calculated using the method of Wildhaber and Schmitt (1996), are presented in Table 13. In our study porewater element concentrations were measured directly and thus we were also able to calculate toxic units directly (Table 14). The two sets of results agree in that Site 24, the only sediment to have an estimated total toxic unit value greater than one, also had the highest measured porewater toxic units. However, in five of the six sediments, the model predicted that sulfides would sequester all or nearly all of the metals, and the model underestimated the measured porewater STU. The most serious error was at Site 4 (Table 14), where the model predicted that all metals would be sequestered, and the measured concentration was twice that which would be predicted to cause toxicity (although no toxicity was actually observed at this site). There was little AVS in Site 24 sediment. At that site the model predicted a somewhat higher STU than the value from

measured concentrations. This site was also not toxic. This may be due to deficiencies in the AVS and toxic units models, or it may also reflect the methodology of pore water collection. When pore water is collected in the field, a very small amount of fines can pass through the filter. These fines can include solid-phase metals bound to sulfides. The fines are removed by filtration prior to acidification of the analytical sample and by centrifugation prior to toxicity testing. However, prior to removal of fines, dissolved oxygen concentrations may increase in the pore waters. This would oxidize sulfides and release metals to the pore water. Thus, we would see small increases in porewater metals concentrations. The porewater extraction method we employed is a preferred method for minimizing the amount of fines in collected pore water (Carr and Chapman 1995). However, some fines do pass through the 8-μm filter, and some sediment types will pass more fines than others. The only porewater samples that contained any sediment visible to the naked eye prior to centrifugation were Sites 4 and 5. The presence of these fines, although they were removed prior to analysis, may be partially responsible for the unexpectedly high concentration of metals in Site 4 pore water.

Table 13. Calculated Toxic Units derived from estimated porewater concentrations of copper, cadmium, lead, zinc, nickel, and arsenic based on Wildhaber and Schmitt (1996).

	Toxic Units						
Site	**Cu**	**Cd**	**Pb**	**Zn**	**Ni**	**As**	**Total**
Site 1	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Site 2	0.00	0.00	0.00	0.00	0.02	0.04	0.07
Site 4	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Site 5	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Site 24	0.02	0.19	3.11	0.01	0.02	0.05	3.40
Site 25	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 14. Toxic Units (measured porewater concentration / USEPA water quality criteria) for copper, cadmium, lead, zinc, nickel, and arsenic. Nickel and copper concentrations were obtained from semiquantitative scan (Table 8). Cadmium, lead, zinc and arsenic concentrations were obtained from quantitative measurements (Table 6).

Site	Cu	Cd	Pb	Zn	Ni	As	Total
			Toxic Units				
Site 1	0.10	0.20	0.24	0.05	0.03	0.16	0.78
Site 2	0.17	0.23	0.12	0.09	0.01	0.08	0.70
Site 4	0.40	0.29	0.86	0.15	0.01	0.12	1.83
Site 5	0.08	0.11	0.08	0.04	0.02	0.30	0.63
Site 24	0.51	0.38	0.81	0.22	0.02	0.02	1.96
Site 25	0.16	0.24	0.30	0.10	0.04	0.04	0.88

Toxicity testing

C. dubia normally reproduces parthenogenetically, producing only fertile female offspring. Reproduction of a large number of male offspring is an indication of stress that can be caused by numerous environmental factors including changing light, temperature, or food (Barnes 1980). Identification of the sex of neonate ceriodaphnids is impossible without undue stress to the organism, so males are sometimes inadvertently included as test organisms. Presence of a large number of males in a test is an indication of a stressed population of test organisms and could invalidate the test. In this study, of 220 ceriodaphnids used in the test, only nine were identified as male. Seven of the nine were identified as having the same parent (all the offspring of that individual were male). Replicates stocked with male ceriodaphnids were excluded from all analyses.

Survival of ceriodaphnids was ≥90% and reproduction was high in the CERC well water, the Hard Recon, in the river waters, and in the upstream sediment (Tables 15 and 16). In the reconstituted river water, survival was somewhat reduced (75%) and reproduction was low compared to other references (8.75 young per female vs 31 - 39). This may stem partly from the fact that two male organisms were stocked into this treatment. Although these replicates were excluded from the analysis, the reduced sample size compromises statistical interpretation. All animals were cultured in this reconstituted river water and the cultures were highly successful. If there was any problem with the reconstituted river water, it occurred after the test was begun. Survival was 100% in the Hard Recon, which was made similarly to the reconstituted river water, but with a higher concentration of salts added, and 100% in the CERC well water procedural control, which was the source water of both the reconstituted river water and the Hard Recon. The chemistry of the reconstituted river water was intermediate between that of these two treatments, and the observed reduction in survival and reproduction in this treatment is therefore inexplicable.

Table 15. Percent survival of non-male *Ceriodaphnia dubia* exposed to sample and control water in a 7-day toxicity test on samples collected in the vicinity of the ASARCO lead refining facility, Omaha, Nebraska. *Ceriodaphnia* identified as male were excluded. MW19 is the groundwater sample from monitoring well 19. SEDx refers to pore waters collected from the various sediment sites. NaCl refers to the sodium chloride reference toxicant treatments and the concentration of NaCl added to reconstituted river water. Hard Recon refers to the reconstituted water made to reflect the water quality of the collected river waters.

Treatment	6.25	12.5	25	50	100
			Dilution		
MW19	78	30	0	0	0
River water 1					100
River water 2					100
SED1					100
SED2					90
SED24					100
SED25					100
SED4		90	89	100	100
SED5					90
Reconstituted river water					75
Hard Recon					100
NaCl			100	40	0
Well					100

Table 16. Mean reproductive output of *Ceriodaphnia dubia* exposed to sample waters and reference waters in a 7-day toxicity test. Reproductive output is the total number of young produced during the test, regardless of the individual's survival. Number of replicates is in parenthesis. Standard error of the mean is in brackets. *Ceriodaphnia* identified as male were excluded. Treatments significantly lower in reproduction than Site 1 and Site 2 are indicated with two asterisks (**). Treatments significantly lower than Site 1, but not Site 2, are indicated with a single asterisk (*). MW19 is the groundwater sample from monitoring well 19. SEDx refers to pore waters collected from the various sediment sites. NaCl refers to the sodium chloride reference toxicant treatments and the concentration of NaCl added to reconstituted river water. Hard Recon refers to the reconstituted water made to reflect the water quality of the river waters.

| Treatment | Dilution | | | | |
	6.25%	12.5%	25%	50%	100%
SED1					33.8 (10) [4.55]
SED2					26.1 (10) [2.28]
MW19	20.56 (9) [5.27]	7.6** (10) [5.17]	0** (10) [0]	0** (10) [0]	0** (10) [0]
River water 1					48.44 (9) [4.5]
River water 2					32.6 (10) [2.9]
SED24					32.4 (10) [2.55]
SED25					15.88* (8) [3.35]
SED4		26.3 (10) [5.51]	32.56 (9) [5.39]	28.12 (8) [5.66]	31.56 (9) [4.83]
SED5					23.5 (10) [3.36]
Reconstituted river water					8.75** (8) [3.95]
Hard recon					38.7 (10) [4.44]
NaCl			1.11** (9) [0.73]	0** (10) [0]	0** (10) [0]
Well					31.2 (10) [2.13]

In the positive controls (2.5, 1.25, and 6.125 parts per thousand sodium chloride), survival was strongly reduced in the two higher concentrations, and reproduction was reduced in all three concentrations. This is within, but near the higher end, of the range of sodium chloride sensitivity seen in other *Ceriodaphnia* tests at our facility.

Survival and reproduction were significantly ($p<0.05$) reduced in all but the lowest dilution (6.25%) of the groundwater sample, compared to the upstream porewater references Sites 1 and 2. Reproduction was not reduced significantly in the lowest concentration of the groundwater sample.

Survival was 100% and reproduction was very high in both river water samples. Survival was ≥90% in all sediment pore waters. Reproduction in pore waters from the two sites associated with the Burt-Izard drain was not significantly reduced (Table 16). Because of *a priori* concerns that Site 4 would be highly toxic, a dilution series was performed on pore water from this site. However, all concentrations, including the 100% porewater concentration, were not toxic. Site 24, which had the highest porewater metal concentrations of any sample, was not significantly different in reproduction from the reference pore waters. Pore water from Site 25 was significantly reduced in reproduction compared to Site 1, but not significantly reduced compared to Site 2. Metals concentrations in Site 25 pore water were somewhat elevated compared to the references, but in no case did the concentrations of measured metals exceed the water quality criteria. The summation of measured porewater metal toxic units at this site was 0.88 (where a value of greater than 1 theoretically would be potentially toxic). Therefore, this site, which may have been marginally toxic, contained marginally high metals concentrations.

We expected groundwater influences on the sediment to be stronger in the Burt-Izard Drain than in the river sites. We did not find this to be so. A strong rain event, such as the one occurring the night prior to the sampling trip, could flush pore water from the large-grained sediments we found within the Burt-Izard drain. The result would be a short-term decrease in toxicity until the pore water regained equilibrium with the sediment particles, or until more groundwater intruded into the sediment at that site. However, this does not appear to have been the case at Site 4, the sampling location lying within the Burt-Izard drain.

Porewater ammonia was somewhat elevated at Site 4 (Table 2), which would not be expected in the case of dilution with rainwater. Also, whole sediment concentrations of most elements were lower at Site 4 (Table 7) than at most other sites. Therefore, sampling directly after a strong rain event does not seem to have been responsible for the lack of toxicity at this site, which would have been the site most likely to be affected by the rain event.

The daily measurements of dissolved oxygen and pH and conductivity associated with the toxicity tests were not remarkable and were not highly variable within treatments. All dissolved oxygen concentrations were at or above 7 mg/L.

Principal components analysis

There are 741 pairs of elements from the sediment data and 465 pairs in the water data, which are too many to list. As should be expected, some elements were strongly correlated with each other, especially in sediment samples. Therefore we made use of principal component analysis to develop a series of indices that summarize the element concentration data; i.e., the principal components are an attempt to develop an index of a sample's elemental composition.

Descriptions of the first three principal components for sediment numbers are listed in Table 17. The first three components account for 73%, 17% and 6% of the sediment data variability, respectively. The first three principal components for water data are described in Table 18. Those components account for 47%, 23% and 11% of the water data variability, respectively. The first sediment principal component is highly correlated with over half of the elements. This is possible since many of those elements were highly correlated to each other. In both cases the first principal component accounts for much of the variation in the data sets. The third principal component has few strong correlations with the element concentrations. In both datasets the principal components 4 and beyond are not meaningful. No strong patterns were obvious except that the first sediment principal component reflects the relatively low concentrations of many elements at Site 4 (Fig.2).

Table 17. Correlation of concentrations of elements found in sediment samples with the first three principal components calculated from those numbers. Correlations with absolute values greater than 0.8 are in bold. Sediments were collected in the vicinity of the ASARCO lead refining facility, Omaha, Nebraska.

Element	PC1	PC2	PC3	Element	PC1	PC2	PC3
Y	**1**	-0.01	0	Co	**0.9**	0.39	-0.08
Li	**1**	0.03	0	Ba	**0.85**	-0.51	-0.1
Pr	**0.99**	-0.03	-0.12	Zr	**0.85**	0.31	-0.38
Tb	**0.99**	-0.02	-0.13	Ti	**0.83**	-0.52	0.16
Al	**0.98**	0.19	-0.03	Dy	**0.82**	0.42	0.39
Er	**0.97**	0.21	-0.08	Mn	0.74	0.62	0.1
Sm	**0.96**	0.10	-0.2	Na	0.62	-0.29	-0.47
Gd	**0.96**	0.10	-0.2	Cd	0.44	**0.79**	0.21
Nd	**0.96**	-0.25	0.02	Pb	0.29	-0.07	**-0.82**
La	**0.96**	-0.25	0.02	Zn	0.29	**0.91**	-0.18
Eu	**0.96**	0.26	0.07	Fe	-0.46	**0.84**	-0.19
Ce	**0.96**	0.12	-0.21	Cu	-0.5	**0.85**	-0.11
K	**0.96**	0.22	0.19	Sr	-0.56	**0.83**	-0.03
Mg	**0.95**	-0.21	0.18	Ni	-0.66	0.63	-0.29
Yb	**0.94**	0.32	0.08	Sb	-0.73	-0.32	-0.53
Ho	**0.93**	0.34	0.08	Ca	**-0.87**	0.48	-0.03
Ga	**0.92**	0.37	0.11	Cr	**-0.89**	0.44	-0.05
Rb	**0.91**	0.32	0.17	Mo	**-0.94**	0.33	-0.05
V	**0.91**	0.21	0.02	Sn	**-0.97**	0.21	-0.01
As	**0.9**	-0.04	-0.42				

Table 18. Correlation of concentrations of elements found in water samples with the first three principal components calculated from those numbers. Correlations with absolute values greater than 0.8 are in bold.

Element	PC1	PC2	PC3	Element	PC1	PC2	PC3
Co	**0.98**	0.06	-0.12	B	0.58	0.31	0.27
Ba	**0.97**	0.23	-0.02	Rb	0.51	0.24	0.1
Br	**0.96**	-0.25	0.01	Mo	0.4	**0.85**	-0.27
Ga	**0.95**	-0.15	-0.18	Zn	0.36	0.71	0.17
Ca	**0.93**	-0.24	0.2	Pb	0.34	**0.83**	-0.16
Cr	**0.92**	0.07	0.22	Sn	0.3	0.45	-0.63
I	**0.91**	-0.08	0.09	Sb	0.08	**0.91**	0.09
Sr	**0.87**	-0.3	0.33	W	0.06	0.7	-0.29
Mn	**0.86**	0.33	0.03	Al	-0.09	**0.86**	0.25
As	**0.86**	-0.01	-0.42	Ce	-0.18	0.68	-0.65
Mg	**0.82**	-0.35	0.4	Cd	-0.26	0.68	0.61
K	0.76	-0.03	-0.09	Cu	-0.27	0.67	-0.16
Fe	0.73	0.08	-0.34	U	-0.62	0.52	0.41
Ni	0.71	0.42	0.45	V	-0.67	0.49	0.51
Na	0.7	-0.32	0.47	Li	-0.78	0.07	0.44
Ti	0.67	0.49	0.42				

There was no strong relationship between *Ceriodaphnia* reproduction and element composition. This is not surprising because, in general, reproductive rates did not differ between sites significantly. In particular none of the principal components adequately explain the low reproductive rates observed at Site 25. Inspection of concentrations of individual element concentrations similarly does not satisfactorily explain the low reproduction at Site 25.

Cluster analysis

Hierarchical cluster analysis was used to evaluate similarities between sites, to see if sites differed in water quality depending on their location in the study. MW19 was excluded from the analysis because its high concentrations of many elements caused undue influence on the analysis.

Figure 3 shows the results for analysis of sediment data and demonstrates that Sites 1 and 2 are very similar in elemental composition, as are Sites 24 and 25. Sites 4 and 5 do not group as closely. This is not surprising, despite their physical proximity, because of the physical differences between these two sites (Table 4). Site 4 also stood out in the principal component analysis since its concentrations of most elements were noticeably lower than those of the other sites.

Figure 4 shows the results for analysis of the water data. Again, the data reflects the layout of the study sites. RW1 and RW2 are quite close together, as are the pairs (Sites 1 and 2) and (Sites 24 and 25). Again, Sites 4 and 5 do not group closely to each other.

Figure 2. Comparison of the first principal component calculated from element concentration data of sediment samples between study sites in the vicinity of the ASARCO lead refining facility, Omaha, Nebraska.
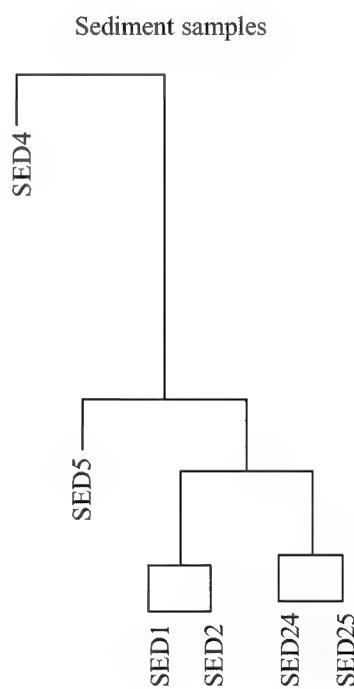
Figure 3. Results of hierarchical cluster analysis of element concentrations measured from sediment samples collected near the ASARCO facility in Omaha, Nebraska

Water samples
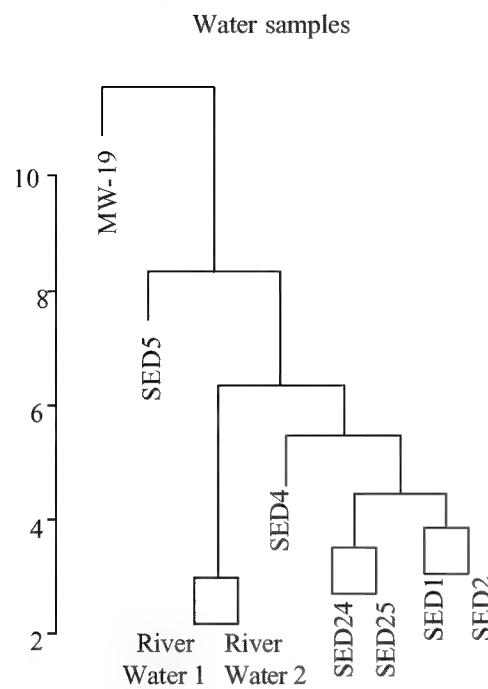
Figure 4. Results of hierarchical cluster analysis of element concentrations measured from aqueous samples collected near the ASARCO facility, Omaha, Nebraska.

Similarity between sites in terms of elemental composition can also be inspected by the use of principal component plots (biplots). These plots simply plot each site in a two-dimensional graph using their first two principal component scores. Figure 5 shows the biplot from sediment samples. The same groupings observed in the cluster analysis are found here. Sites 1 and 2 fall very close to each other. Sites 24 and 25 are also fairly close, especially in respect to the first principal component. Sites 4 and 5 are separated. Figure 6 shows this pattern one more time in the water data, with the addition of RW1 and RW2 being fairly close to each other. In summary, the cluster analysis shows us that samples that were similar in location and in type were also similar in water quality and in elemental composition at the time and under the hydrologic conditions that they were sampled. This is not surprising, but does serve as verification that sampling was correctly conducted and that sediments and sediment porewater chemistry varied according to location.

Sediment samples

Figure 5. Biplot of element concentration data measured from sediment samples.
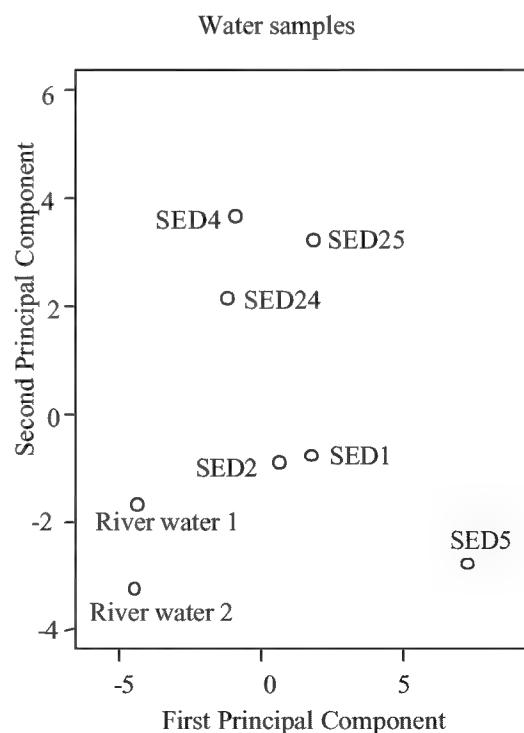
Water samples

Figure 6. Biplot of element concentration data measured from water samples.

Conclusions

Water quality variables of surface and sediment pore water, including dissolved oxygen, hardness, alkalinity, temperature, pH, ammonia, sulfate, nitrate+nitrite, chlorides, and calcium, were clearly within acceptable limits for *Ceriodaphnia dubia* growth and reproduction.

The groundwater from the monitoring well (MW19) was highly toxic, and high in many toxic elements. It had to be diluted to a concentration of 6.25% with reconstituted river water before survival and reproduction were not significantly different from the references. Although this study was not intended to encompass the dilution rate of groundwater with river and sediment pore waters *in situ*, one would surmise that groundwater would be quickly and highly diluted (i.e., to <6.25%) as it enters the Missouri River.

Metals of toxicological concern were not highly elevated in sediments, sediment pore waters, or river waters. At the one site where lead was somewhat elevated in the sediment (Site 25), it was present in the pore water at a concentration of less than one-third of the USEPA chronic criteria for surface waters. *Ceriodaphnia* reproduction may have been somewhat impaired at this site. Using the toxic units approach, based on measured porewater concentrations, metals concentrations in pore water at this site approached but did not exceed the concentration where chronic toxicity might be expected. Perhaps these marginally high concentrations of metals impacted *Ceriodaphnia* reproduction, or other unmeasured contaminants, such as organic chemicals, may have been involved. The reduction in reproduction was not clearly significant.

Sediments in large rivers such as the Missouri are in a constant state of flux; they are deposited, re-suspended, and transported continuously. Transport of sediment in rivers is well-studied (Meade et al. 1990). Sediments that were present in the early spring were completely removed by higher flows before the fall sampling trip. Much of the substrate on the ASARCO waterfront was solid slag at the time of the sampling trip. Weathering of slag and movement of groundwater should provide a constant source of lead and other contaminants from this site. However, the dilution factor of the Missouri River is immense, and

apparently sediment does not linger long at the site before passing on downstream. A prolonged period of low flow could cause sediments to remain in place long enough for contaminants from the ASARCO site to reach toxic concentrations along the waterfront. However, the United States Army Corps of Engineers maintains regular, annual periods of high flow for barge traffic on the river. Sediment accumulating during the winter low flow period apparently washes away during the following navigation season.

Our intent was to perform this study after a prolonged low-flow period. Under such conditions, the net flow of groundwater from the ASARCO Omaha facility is most likely to be toward the Missouri River, and pore waters collected under such conditions would contain higher concentrations of groundwater originating from the ASARCO facility. During or following high water periods, the pore waters are more likely to be dominated by river water. Even after equilibration with the sediments, such pore waters would be expected to have much lower elemental concentrations than groundwater from the site. Unfortunately, the need for the data and information presented in this report necessitated that we conduct the study in the early fall of 1998, following a summer-long high water period resulting from record snowfall during the winter of 1997-1998. Therefore, groundwater adjacent to the river may have been dominated by river water at the time of sampling.

This contention is supported to a degree by earlier monitoring data for MW19, the one we sampled and tested. This well is the one closest to the Missouri River and therefore the one likely to be most influenced by river water. Monitoring samples taken between August of 1995 and January of 1998 had concentrations of calcium, chlorides and sulfates averaging 2 to 5.3 times higher than they were during our study (Table 19). It could be that groundwater had in fact been diluted by river water prior to our arrival. However, the chloride concentration of MW19 water was over five times that of the river water during this study, and the concentration of arsenic found in the water taken from MW19 (574 μg/L), was very close to the historical average arsenic concentration (598 μg/L, Table 19).

Table 19. Historical water quality of monitoring well 19 (MW19) and water quality of MW19 when sampled in this study (October 5, 1998). Historical water quality from unpublished data provided to USEPA by the Nebraska Department of Environmental Quality. All values in mg/L.

Date	Calcium	Chloride	Sulfate	Arsenic
Aug. 1995	431	1396	789	0.260
Mar. 1996	507	1484	1235	0.770
May 1996	442	1709	1167	0.390
Jan. 1997	414	1588	979	0.660
May 1997	272	1136	864	0.680
Jan. 1998	195	1003	900	0.830
Historical average	**377**	**1386**	**989**	**0.598**
Oct. 1998 (this study)	185	321	186	0.574

In this study, we found measurable concentrations of metals in pore waters that, according to the Toxic Units model of Wildhaber and Schmitt (1996), should have had virtually all metals bound to sulfides and therefore not present in the pore water. This disagreement may have been due to deficiencies in the model or due to release of metals by oxidation of sulfides attached to sediment particles that were not immediately removed by the porewater extraction technique. The Wildhaber and Schmitt model (using measured porewater concentrations) predicted that two sites would be toxic, but no toxicity was observed at those sites.

Acknowledgements

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13. ABSTRACT (Maximum 200 words)

This study is an evaluation of the potential environmental impacts of contaminated groundwater from the ASARCO metals refining facility adjacent to the Missouri River in Omaha, Nebraska. Surface waters, sediments, and sediment pore waters were collected from the Burt-Izard drain, which transects the facility, and from the Missouri River adjacent to the facility. Groundwater was also collected from the facility. Waters and sediments were analyzed for inorganic contaminants, and the toxicity of the waters was evaluated with the *Ceriodaphnia dubia* 7-day test. Concentrations of several elemental contaminants were highly elevated in the groundwater, but not in river sediment pore waters. Lead concentrations were moderately elevated in whole sediment at one site, but lead concentrations in pore waters were low due to apparent sequestration by acid-volatile sulfides. The groundwater sample was highly toxic to *C. dubia*, causing 100% mortality. Even at the lowest groundwater concentration tested (6.25%) *C. dubia* survival was reduced; however, at that concentration, reproduction was not significantly different from upstream porewater reference samples. Sediment pore waters were not toxic, except reproduction in pore water collected from one downstream site was somewhat reduced. The decrease in reproduction could not be attributed to measured elemental contaminants.

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